The Development of Nano-Composite Electrodes for Natural Gas-Assisted Steam Electrolysis for Hydrogen Production

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Objectives

The objective of this work is to develop a fundamental understanding of how interactions between the various metal-oxide and metal components in the electrodes of solid-oxide electrolyzers (SOE) affect catalytic and electrochemical performance and to use these insights to design nanocomposites with unique materials properties for this application. Important scientific questions being addressed include: How does one stabilize layered materials (e.g. Cu- coated Co and $La_{0.8}Sr_{0.2}FeO_3$- coated yttria-stabilized zirconia) under both oxidizing and reducing conditions; how can reaction barriers be minimized for desired electrochemical reactions while maintaining barriers for undesired reactions (e.g. CH_4 oxidation vs. CH_4 decomposition to coke); what materials properties influence SOE electrode polarization; how are materials affected by cathodic and anodic polarization?

Technical Barriers

A better understanding of materials interactions in SOE should lead to higher electrolyzer efficiencies. It could also lead to improved methods for producing H_2 by Natural Gas Assisted Steam Electrolysis (NGASE).

Abstract

A variety of novel air and fuel electrodes have been developed and tested for solid-oxide electrolyzers (SOE) and NGASE devices. In all cases, the electrodes are made by addition of the active, electrode components into porous yttria-stabilized zirconia (YSZ) layers that had been pre-sintered with the YSZ electrolyte. Air electrodes based on Sr-doped $LaFeO_3$ (LSF) have been shown to exhibit superior performance to more traditional LSM-based electrodes but can deactivate after long times or high temperatures, apparently due to sintering of the LSF. Cu-based electrodes were found to exhibit poor thermal stability above 1,073 K due to sintering of Cu, but Cu-Co electrodes prepared by Co electrodeposition onto the Cu composite had significantly improved performance. It was shown that a Cu monolayer forms at the Co surface after heating in H_2 due to free-energy considerations, so that the Cu-Co electrodes exhibit the thermal stability of Co and the chemical stability of Cu. Finally, a novel, all-ceramic electrode was developed for use in fuel environments. The ceramic electrode consists of a thin functional layer optimized for catalytic activity with a thicker conduction layer.

Progress Report

First, we demonstrated that it is possible to take a traditional, Ni-cermet electrode, and coat it with a second metal to prevent carbon formation when the electrode is exposed to dry methane. In this work, we demonstrated that one can electroplate Cu onto a normal Ni-YSZ electrode and that the presence of plated Cu completely suppressed carbon formation, at least initially. Unfortunately, Cu-Ni alloy formation led to Ni appearing at the surface after high-temperature treatments. Our investigations of the electroplating process allowed us to determine when mass transfer limitations or drops in the potential of the electroplating solution would result in an uneven distribution of Cu. We demonstrated that we could prepare a Cu-coated Ni-YSZ cermet electrode and operate it as a fuel-cell anode. The performance in dry methane was modest but no attempt was made to add catalytic function to the electrode to dissociate C-H bonds.

Second, we demonstrated that we could enhance the thermal stability of an impregnated Cu-based electrode by electroplating Cr onto Cu-based electrodes. The addition of Cr had no effect on the electrode performance as an SOFC anode at 973 K in humidified H_2, but significantly improved the thermal stability. Without Cr, SEM showed structural changes in the Cu films after heating to 1,173 K resulting in increased ohmic resistances in impedance spectra of the electrode. The addition of Cr increased thermal stability so that the electrodes were unaffected by heating to 1,173 K in dry H_2. Some oxidation of Cr was observed by

XRD following exposure of the composite to 80% H_2-20% H_2O mixtures at 973 K for 20 h, but partial oxidation of Cr did not affect the thermal stability of the electrode. Exposure of the composite to 80% H_2-20% H_2O mixtures at 1,173 K for 20 h resulted in complete oxidation of the Cr and a loss of enhanced thermal stability. Attempts to prevent Cr oxidation by electrodeposition of Cu onto the Cr were unsuccessful. While the propensity of Cr to undergo bulk oxidation under electrode conditions suggest that it will not be a good candidate for stabilization of Cu, the work with Cr does demonstrate the validity of the concept of using a coated electrode for enhanced thermal stability.

Cu-based, solid oxide fuel cell (SOFC) and electrolyzer (SOE) electrodes were also modified by electrodeposition of Co. The addition of only 5-vol% Co by electrodeposition significantly improved the thermal stability compared to either Cu-ceria-YSZ, Cu-Co-ceria-YSZ, or Co-ceria-YSZ electrodes prepared only by impregnation with much higher metal loadings, demonstrating that electrodeposited metal layers form metal films with better connectivity. In the absence of Co, SEM showed structural changes in the impregnated Cu after heating to 1,173 K in humidified H_2 and these changes caused large increases in the ohmic resistance of fuel cells, as measured by impedance spectroscopy. In contrast, the ohmic resistance of a cell with 13-vol% Cu, 9-vol% ceria, and 5-vol% Co increased only slightly after 48 h at 1173 K in humidified H_2. While a Co-ceria-YSZ composite was found to form large amounts of carbon upon exposure to dry CH_4 at 1073 K for 3 h, the Co-Cu-ceria-YSZ composites did not form measurable amounts of carbon for the same conditions. XPS results for a Cu foil with a 250-nm Co film demonstrated that Cu migrates to the surface of the Co upon heating above 873 K, forming a stable Cu layer that appears to be approximately one monolayer thick.

A new concept was also developed for high-performance, all-ceramic electrodes. It was shown that good electrode performance could be achieved by using a very thin, catalytically active functional layer, with a non-catalytic conduction layer. An electrode impedance of 0.26 $\Omega.cm^2$ was obtained at 700°C in humidified H_2 using a Ag-paste conduction layer and a 12-μm thick functional layer made from 1-wt% Pd and 40-wt% ceria impregnated into YSZ. Replacing the Ag paste with a 100-μm layer of porous $La_{0.3}Sr_{0.7}TiO_3$ (LST) had minimal effect on electrode performance. Pd was shown to be crucial for obtaining good performance, especially when operating cells in dry CH_4. The electrode concept is flexible and allows various materials to be used in the functional and the current-collector layers.

We also have examined composite electrodes of yttria-stabilized zirconia (YSZ) with $La_{0.8}Sr_{0.2}MnO_3$ (LSM), $La_{0.8}Sr_{0.2}FeO_3$ (LSF), and $La_{0.8}Sr_{0.2}CoO_3$ (LSCo) to understand their performance characteristics as solid oxide electrolyzer (SOE) anodes in comparison to their performance as solid oxide fuel cell (SOFC) cathodes at 973 K. The LSM-YSZ electrode was activated by cathodic polarization but the enhanced performance was found to be unstable during electrolysis, with the electrode impedance increasing to near its un-enhanced state after 24 h. LSF-YSZ and LSCo-YSZ electrodes exhibited a nearly constant impedance, independent of current density, during both SOE and SOFC operation. The performance of an LSF-YSZ composite for electrolysis current densities above 200 mA/cm^2 was unaffected by changing the O_2 partial pressure from ~10^{-2} atm to 1 atm, while the lower O_2 pressure harmed the performance of the LSCo-YSZ composite.

Due to the outstanding performance of LSF-YSZ electrodes, we further examined their performance as a function of time and calcination temperature. X-ray diffraction (XRD) patterns of the LSF-YSZ composites indicated an expanded lattice parameter after calcination above 1,523 K, suggesting Zr reacted with the LSF to form a Zr-doped perovskite; but XRD provided no evidence for reaction between LSF and YSZ after calcination at 1,373 K or after operation for 1,000 h at 973 K and 700 h at 1,073 K. Furthermore, a composite of 40-wt% $La_{0.8}Sr_{0.2}Fe_{0.9}Zr_{0.1}OB_3$ in YSZ showed reasonable performance at 973 K, with an area-specific resistance (ASR) of 0.22 $\Omega \cdot cm^2$, so that this is not believed to be an important mechanism for deactivation. Based on symmetric-cell measurements, electrodes calcined at 1,123 K showed an initial ASR of 0.13 $\Omega \cdot cm^2$ at 973 K but this increased linearly with time to 0.55 $\Omega \cdot cm^2$ after 2,500 h at 973 K. However, the ASR depended strongly on current density, decreasing dramatically under both anodic and cathodic polarization. Electrodes calcined at 1373 K showed an ASR of 2.5 $\Omega \cdot cm^2$ at 973 K but this value also decreased dramatically under polarization. Scanning electron microcopy (SEM) images demonstrate that aging at 973 K and calcination at 1,373 K cause significant sintering of the LSF. It is therefore suggested that deactivation is caused by morphological changes, rather than solid-state reactions, with a dense layer of LSF forming over the YSZ substrate. Methods for forming stable electrodes by changing the morphology of the YSZ are suggested.

Finally, porous composite anodes consisting of a YSZ backbone that was impregnated with CeO_2 and various amounts of metallic components including Cu, Co and Pd were fabricated. The performance of these electrodes was then tested in a solid oxide water electrolysis cell under conditions where the anode was exposed to the reducing gasses H_2, CH_4 and CO. The reducing gasses were used to decrease the electrochemical potential of the cell and increase overall efficiency. The results of this study show that Cu-CeO_2-YSZ anodes have low catalytic activity for the oxidation of CO and CH_4 and are not very effective in lowering the cell potential while operating in the reducing gas assisted mode. The addition of Co to the Cu-CeO_2-YSZ anode resulted in a modest increase in the catalytic activity and enhanced the thermal stability of the anode. A Pd-C-CeO_2-YSZ anode was found to have the highest catalytic activity of those tested and gave the largest reductions in the operating potential of the solid oxide electrolysis cell.

Future Directions

Future research will focus in four directions: 1) Improved manufacturability by electroplating metals on carbon-deposited YSZ; 2) Improved thermal stability with ceramic electrodes; 3) An examination of mixed-conducting electrolytes for improved electrolysis efficiencies; 4) Studies of the effect interfaces have on electrode morphology. A major hurdle in the acceptance of "impregnated" electrodes is the tediousness of fabrication. We are presently depositing carbon layers over the porous YSZ and electroplating metals onto the carbon. Because the electronic conductivity of the functional layers in our ceramic anodes comes from ceria deposits that are prone to sintering, we are attempting to replace the YSZ framework of the impregnated electrodes with composites of YSZ (for ionic conductivity) and LST (for electronic conductivity). Based on the findings of a start-up company (CTP Hydrogen, www.ctphydrogen.com), we will investigate the effect on the electrodes of having mixed-conducting electrolytes. CTP has recently developed a similar concept to NGASE but replaced the YSZ electrolyte with a mixed-conducting composite of YSZ and LST. While this design does not allow an electronic potential to be placed across the electrodes, the concept is very attractive in that the electrolyzer is extremely simple and very robust, allowing pure H_2 to be produced from almost any hydrocarbon fuel in a single step. Because only minimal electrode conductivity is required with mixed-conducting electrolytes, the design requirements for this system change significantly. Finally, we have used AFM to show that a YSZ substrate can affect the morphology of supported LSM particles. We believe this may well explain the activation and deactivation processes observed with LSM-YSZ electrodes and lead to improved air electrodes for SOE.

Publications Citing DOE Support

1. "Electrodeposition of Cu into a Highly Porous Ni/YSZ Cermet", S. Jung, M. D. Gross, R. J. Gorte, and J. M. Vohs, Journal of the Electrochemical Society, 153 (2006) A1539-43.

2. "Enhanced Thermal Stability of Cu-Based, SOFC Anodes by Electrodeposition of Cr", M. D. Gross, J. M. Vohs, and R. J. Gorte, Journal of the Electrochemical Society, 153 (2006) A1386-90.

3. "A Comparison of LSM, LSF, and LSCo for Solid Oxide Electrolyzer Anodes", Wensheng Wang, Yingyi Huang, Sukwon Jung, John M. Vohs, and Raymond J. Gorte, Journal of the Electrochemical Society, 153 (2006) A2066-70.

4. "A Study of Thermal Stability and Methane Tolerance of Cu-Based SOFC Anodes with Electrodeposited Co", M. D. Gross, J. M. Vohs, and R. J. Gorte, Electrochimica Acta, 52 (2007) 1951.

5. "A strategy for achieving high-performance with SOFC ceramic anodes", M. D. Gross, J. M. Vohs, and R. J. Gorte, Electrochemical and Solid State Letters, 10 (2007) B56.

6. "Impedance characterization of a model Au/YSZ/Au electrochemical cell in varying oxygen and NO_x concentrations", L. Y. Woo, L. P. Martin, R. S. Glass, and R. J. Gorte, Journal of the Electrochemical Society, accepted.

7. "The Stability of LSF-YSZ Electrodes Prepared by Infiltration", W. Wang, M. D. Gross, J. M. Vohs, and R. J. Gorte, Journal of the Electrochemical Society, accepted.

8. "Multilayer High Performance Ceramic Anodes", M. D. Gross, R. J. Gorte, and J. M. Vohs, ECS Transactions - Solid Oxide Fuel Cells, Volume 7, accepted.

9. "Hydrogen Production via CH_4 and CO Assisted Steam Electrolysis", W. Wang, J. M. Vohs, and R. J. Gorte, Topics in Catalysis, accepted.

10. "An examination of SOFC anode functional layers based on ceria in YSZ", M. D. Gross, J. M. Vohs, and R. J. Gorte, submitted.

11. "High-Performance Ceramic Anodes for Use with Strategic and Other Hydrocarbon Fuels", R. J. Gorte, J. M. Vohs, and M. D. Gross, patent claim submitted.